AN ELECTRODYNAMIC BALANCE AND A NEW LIQUID OXYGEN CRYOSTAT FOR MEASUREMENT OF MAGNETIC SUSCEPTIBILITIES BETWEEN 400°K AND 60°K.

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ABSTRACT A highly accurate and sensitive electrodynamic balance of robust construction for the measurement of magnetic susceptibilities of single crystals, powdered samples and liquids has been described. The balance uses an electrodynamic compensation of magnetic force and photoelectric magnification of deflection, avoids many sources of errors and troubles and gives an accuracy better than 0.1%. A new cryostat providing an extremely fine control of temperature, with the help of some special devices, is incorporated with the balance to work between 400°K and 63°K, using liquid oxygen as coolant and is described in detail. The calibrations of the balance and the thermo-couple have been compared against the existing London and Calcutta measurements on standard paramagnetic substances, e.g., Cr^{+3} alum, Fe^{+3} alum.

INTRODUCTION

In the study and measurement of the principal magnetic susceptibilities of crystals, a number of difficulties such as accurate calibration of field, location and orientation of the crystals, maintenance of steady temperature balancing the magnetic force etc. limits the accuracy of the data to within ~1%. To estimate the anisotropies of the crystals of the order of 5 to 30% of the mean susceptibilities with sufficient accuracy, the above limit should be pushed back to about 0.1% or less. The present paper describes a modified Curie-balance of robust construction designed to measure susceptibilities of crystals as well as powders and liquids down to 60°K, and uses a new electrodynamic compensation of the magnetic force and photoelectric magnification of deflection. The temperatures between 400°K and 60°K are maintained accurately using a new cryostat with liquid oxygen as coolant and a vacuum jacket with a heater element as a temperature compensating device.

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A SURVEY OF OLDER METHODS

Most of the usual methods for measuring susceptibilities consist of estimating the translational force on a sample placed in an inhomogeneous magnetic field. For example, in the original Curie method (1895) the horizontal translational magnetic force on a small sample fixed at one end of a balance arm, suspended from the midpoint with a fine fibre, is balanced against the torque of the fibre. In the Gouy Method (1889) the vertical pull on a long sample suspended from one arm of an analytical balance is compensated by weights on the other arm. In the Sucksmith's ring balance (1929), the vertical pull on a small sample is balanced against the bending moment of a phosphor bronze ring from which the sample is suspended In the Foex-Forrer balance (1936), the horizontal magnetic force on the sample mounted at one end of a horizontal beam, which is suspended with double bifilar strings, is compensated by the electrodynamic force exerted between a current-bearing coil carried on the moving system and a fixed permanent magnet. The quartz fibre torsion microbalance of Bose (1947) with its arrangement of suspending the crystal from one end of the beam with a fine quartz fibre is very delicate, but rather unstable and hence difficult to handle. The Curie-type torsional balance of Dutta Roy (1955) eliminates many sources of errors. But besides powdered and liquid samples, only single crystals of axial symmetry can be measured with it. Moreover, the manual operation of torsion head causes vibration of the system.

All the above balances excepting the Curie types are inherently gravity controlled and hence have low deflection sensitivity in order to be sufficiently stable, and excepting the microbalance type none is suitable for single crystals. Most of these are so delicately suspended that it is a great strain upon the worker to handle them and external disturbing factors and zero shifts often make it impossible to have reproducible values

Considering all these facts, a balance was constructed, avoiding the defects and utilizing the points of advantages of the earlier instruments as far as possible. To avoid gravity control a Curie method was chosen. For the sake of sensitivity, a null type instrument rather than a deflection type instrument was decided upon For the sake of ease of manupulation and robust construction, fragile quartz fibre suspension was replaced by metallic strip. Vibrations and consequent uncertainty due to manual operation were eliminated by the technique of remote controlled electrodynamic restitution.

THEORY OF THE METHOD

The l-th component of the force acting on a single crystal of volume v placed in a magnetic field H is given by

$$|F_l| = v \sum_{ij} k'_{ij} H_i \frac{\partial H_j}{\partial x_l} \quad (i, j, l = 1, 2, 3) \qquad \ldots \quad (1)$$

where $|H_i|$ is the component of field along x_i axis. k'_{ij} is ijth component of the volume susceptibility tensor with reference to any arbitrary set of axes x_1, x_2, x_3. Expressing the susceptibility tensor in terms of a set of axes X_1, X_2, X_3 fixed in the crystal, conveniently chosen as the principal axes of the susceptibility ellipsoid, we have only three non-vanishing components. The relation between k and k' is given by

$$k'_{ij} = \sum_{\alpha=1}^{3} k_\alpha \frac{\partial X_\alpha}{\partial x_i} \cdot \frac{\partial X_\alpha}{\partial X_j} \qquad \ldots \quad (2)$$

Substituting in equation (1),

$$F_l = v \sum_{\alpha} \sum_{ij} k_\alpha \frac{\partial X_\alpha}{\partial x_i} \cdot \frac{\partial X_\alpha}{\partial x_j} H_i \frac{\partial H_i}{\partial k_l} \qquad \ldots \quad (3)$$

In our present experimental arrangement, the pole pieces are so shaped as to produce a horizontal field with a horizontal gradient, x_3 being taken as the vertical direction. The single crystal is suspended from a very thin fibre from one arm of a modified Curie balance to be described later, with k_3 vertical, leaving the crystal free to rotate in the horizontal plane. Assuming $k_1 > k_2$, X_1 axis of the crystal will set parallel to the field H, neglecting the very small torsion of the fibre. X_2 and X_3 directions being perpendicular to H, K_2 and K_3 will have no contribution to the force. Now

$$H_1 = H \frac{\partial x_1}{\partial X_1}, \quad H_2 = \frac{\partial x_2}{\partial X_1}, \quad H_3 = 0 \qquad \ldots \quad (4)$$

or
$$H = H_1 \frac{\partial X_1}{\partial x_1} + H_2 \frac{\partial X_1}{\partial x_2}$$

Therefore denoting the direction of the field gradient as simply x

$$\frac{dH}{dx} = \frac{\partial H_1}{\partial x} \cdot \frac{\partial X_1}{\partial x_1} + \frac{\partial H_2}{\partial x} \cdot \frac{\partial X_1}{\partial x_2} \qquad \ldots \quad (5)$$

From equations (4) and (5),

$$\sum_{ij} \frac{\partial X_1}{\partial x_i} \cdot \frac{\partial X_1}{\partial x_j} H_i \frac{\partial H_j}{\partial x} = H \frac{dH}{\partial x} \qquad \ldots \quad (6)$$

Eq. (3) therefore reduces to

$$F = vk_1 \cdot H \frac{dH}{dx} \qquad \ldots \quad (7)$$

The derivation clearly indicates that the field direction and the gradient direction need not be exactly perpendicular as required in certain earlier methods. In the experimental arrangement, the force on the sample is exactly balanced by the force exerted on a small vertical coil, rigidly attached to the balance beam, placed close to the sample with its axis as nearly parallel to the field direction as possible, and carrying a suitable electric current C. This force due to the field on the coil

$$F' = nAC \frac{dH}{dx} \cos\theta \qquad \ldots \quad (8)$$

where, n = number of turns in the coil

A = mean area of a turn

θ = small angle between the axis of the coil and the field.

For balancing, $F = F'$

or
$$vk_1 \left(H \frac{dH}{dx} \right)_{sample} = nAC \left(\frac{dH}{dx} \right)_{coil} \cos\theta \qquad \ldots \quad (9)$$

In general the suspended system including the coil, the suspension rod the sample holder if any, will experience a pull even in the absence of any magnetic sample To balance this pull, we must employ an "initial current" C_0 through coil. Also we must take into account the susceptibility k_0 of the surrounding medium Correcting for these, eq. (9) becomes

$$v(k_1 - k_0) \left(H \frac{dH}{dx} \right)_{sample} = nA(C - C_0) \left(\frac{dH}{dx} \right)_{coil} \cos\theta \qquad \ldots \quad (10)$$

or, expressing in terms of mass susceptibility

$$m \left(\chi_1 - \frac{K_0}{\rho} \right) \left(H \frac{dH}{dx} \right)_{sample} = nA(C - C_0) \left(\frac{dH}{dx} \right)_{coil} \cos\theta \qquad \ldots \quad (11)$$

where m is the mass and ρ the density of the sample. For the calibration of the balance a standard substance of known susceptibility is used. If the volume of the standard sample is nearly the same as that of the experimental sample so that the integrated value of $\left(H \frac{dH}{dx} \right)_{sample}$ per unit volume is the same for both, we get :

$$\frac{m(\chi_1 - k_0/\rho)}{m_s(\chi_s - k_0/\rho_s)} = \frac{C - C_0}{C_s - C_0}$$

$$\chi_1 = \frac{C_1 - C_0}{C_2 - C_0}\left(\chi_s - \frac{K_0}{\rho_0}\right)\cdot\frac{m_s}{m} + \frac{K_0}{\rho} \qquad (12)$$

where the subscript s refers to the standard substance. χ_2 and χ_1 can either be calculated from anisottopy data, or they can be measured directly as above. Obviously, similar relation will also hold good in the case of the mean susceptibility $\bar{\chi}$, for a liquid or powder specimen

DESCRIPTION OF THE BALANCE ASSEMBLY

A preliminary note on the balance was earlier published by Ghosh (1961). Several substantial improvements upon that have been made in the present construction. Basically, the instrument is of the Curie-type, the movement of the arm being restricted to a horizontal plane. It consists (Fig. 1) of a horizontal light

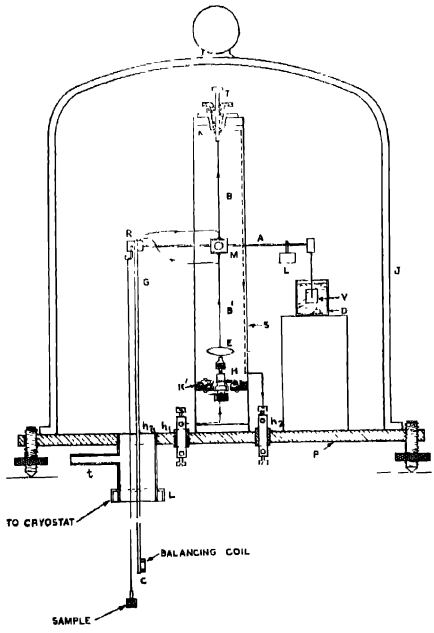

Fig. 1

glass beam A, kept tautly suspended at the middle with moderately fine vertically stretched phosphor-bronze strips. The upper strip B is soldered to a torsion head T used for adjusting the position of the beam, whereas, the lower one B' terminates in an elliptic spring E secured to a universal adjustable holder H which can be rotated, or moved up and down or sidewise so that the torsion on the upper strip can be released, the tension of the suspension can be adjusted or the strips can be lined up vertically. The torsion head and the holder are fixed to ebonite blocks K, K' held in a supporting brass pillar S

A small perspex block R has one horizontal hole which fixes it to balance beam, another vertical hole takes a long thin glass tube G, at the lower extremity of which is attached the electric balancing coil c with its plane vertical and perpendicular to the magnetic field. The attachments are made rigid with araldite cement. The coil comprises of 50 turns of 42 s w g enamelled copper wire wound over a cylindrical thin walled pyrex glass 'former' tube of about 9 mm external diameter and about 2mm. length and impregnated with araldite cement to give high insulation as also rigidity The electric lead to the coil pass through the supporting glasstube and are soldered one to each of the phosphor bronze strips The phosphor bronze strips thus serve a double purpose, they act as suspension wires, as well as electric connections of the coil

A damping vane V made of thin mica sheet, dipping in a dashpot D of apiezon diffusion pump oil fixed to the other end of the glass beam effectively damps out all spurious vibrations. The brass upright support S that holds the balance assembly, is mounted on a flat circular brass base plate P, resting on three levelling screws A greased ground bell-jar J forms a convenient cover for the balance assembly Three holes are drilled in the base plate. In two of these h_1, h_2 are two ebonite blocks with binding terminals, sealed vacuum tight with araldite, for leading in the coil current. The terminals are connected with the phosphor bronze strips. The third aperture h_3 about 2 5 cm in diameter is fitted with a brass collar L taking the glass tube extension of the experimental chamber Joints of the tube are sealed vacuum tight with picien sealing wax. The glass tube carrying the balance coil and the fine fibre carrying the specimen hang side by side in the experimental tube enclosed in the cryostat, placed between the pole pieces of an electromagnet. A side tube t allows the balance chamber and the experimental chamber to be evacuated or filled with dry air through a drying tower system or with any gas as desired.

MOUNTING THE SPECIMEN

The sample is suspended by a fine unspun silk fibre from a hook embedded in the perspex blocks, to which the balancing coil assembly is also attached. If the sample is in powder (or liquid) form it is packed in a small round glass capsule fitted with a miniature ground glass stopper to which the fibre is attached. If

it is a single crystal, a small piece of thin glass rod is fixed to it along one of the principal magnetic axes and the silk fibre attached to the glass rod When placed in proper position, the sample stands clear of the coil and of the side walls of the chamber, so that it is free to rotate about the vertical axis The advantage of this method of mounting is obvious for a single crystal specimen, in which two principal susceptibilities are now contained in the horizontal plane and on applying a horizontal magnetic field, the principal axis corresponding to the greater susceptibility value automatically aligns itself parallel to the field direction Thus one principal susceptibility value can be directly known (cf. Bose, 1947). It is found that in spite of the flexible suspension, there is no appreciable linear motion between the sample and the beam Even if it is there to a small extent, the maximum direction of susceptibility still sets along the direction of the field, and the magnetic pull being always horizontal, no other restoring force except that due to the rigidity of the phosphor-bronze strip exists

In the present Curie-balance set up the gradient and hence the motion of the specimen being in the horizontal plane, the restoring force arises only from the torsional rigidity of the suspension strip, so that the sensitivity of deflection can be made large without considerable sacrifice of stability, unlike the micro-balance type in which gravity is the major controlling as well as stabilizing factor Again here change in the weight of the sample due to deposition of frost or loss of water etc. during measurement will not be recorded as a change in magnetic pull

The Sucksmith form of pole-pieces (Sucksmith, 1939) is adopted as it is the simplest design to obtain the quantity $H \frac{dH}{dx}$ fairly constant over a considerable volume. This ensures that small differences in the position of the different samples will not affect the accuracy of calibration. The magnet is fed by a highly stabilized 15 KW 220 V D C. generator The current is read on an accurate 15 cm. mirror dial ammeter with a magnifying eyepiece. A fine screw rheostat is used to regulate the value of the current and a commutator is provided to reverse the direction of the current several times after each measurement. With a pole gap of 6 cm., required to accommodate the cryostat, the magnet produces a field of 2500 oersteds with a gradient of about 15 oersteds/cm at 1.5 amperes.

DETECTION SYSTEM

The use of phosphor-bronze strip for suspension results in a very small overall deflection of the system This is desirable in several respects. But on the other hand, this necessitates a very sensitive detection system. In practice, a spot of light from a 36 watt 6 volts lamp, fed from a stabilized D. C. generator after collimation and reflection from a mirror fixed at the centre of the balance beam, illuminates nearly equally a pair of photoelectric cells connected in opposition

by a bridge arrangement through a sensitive galvanometer. When the balance beam is in the null deflection position, the resistance of the bridge is adjusted until there is no deflection of the galvanometer. But, when there is a small deflection of the balance beam, the spot shifts more on one cell, thus destroying the balance and a large deflection of the galvanometer is observed. By this means a magnification of the balance beam deflection of nearly 500 times is easily obtained. It can be increased even further by increasing the intensity of illumination

The photocells are mounted side by side in a wooden box painted black inside with a small aperture to admit the light, the cells being located at the farthest end of the aperture A screw motion is provided at the back to shift the position of the photocells slightly, if necessary

MEASURING SYSTEM

Current to energise the compensating coil is taken by suitably tapping a 200 ohms variable potentiometer type wire-wound resistance connected in series with a six volt lead accumulator of 1 25 ampere hour capacity. The variable tapping is necessary for measuring samples of different orders of susceptibility value Three variable resistances of 2500 ohms, 500 ohms and 10 ohms connected in series with compensating coil are employed to provide coarse, medium and fine controls of the current, respectively A switch starts and stops the current while a commutator controls its direction to balance para- or dia-magnetic samples. Three precision wire-wound manganin resistances of 500, 1000 and 1500 ohms with potential tappings are included in series with the coil, the potential drops across any one or more of which can be measured with an accurate potentiometer giving results correct upto 2 microvolts. The same galvanometer which is used with the photocells, can be connected by a throw-over switch to the potentiometer circuit when desired

In actual measurements, the galvanometer is first connected to the photocells, after the sample is placed in position The position of the galvanometer light spot is noted When the magnetic field is switched on, the light spot is observed to move away. Now the current in the balancing coil is started and adjusted first with coarse, then medium and finally with fine controls, till the galvanometer spot comes back to its original position. The galvanometer is then connected to the potentiometer circuit and the potential drop across the desired standard resistance is measured by comparing against a Weston standard cell. The temperature is measured with a calibrated copper-constantan thermocouple using the same potentiometer with a throw-over switch arrangement. The susceptibility is calculated from eqn. (12) by calibrating with a standard substance and knowing the initial current.

REPRODUCIBILITY AND ACCURACY

To test the Reproducibility of the balance the following procedure was adopted. The 'initial' current C_0 was determined Then a crystal of chromium potassium sulphate alum prepared from Merck's G R quality reagent was suspended and balancing current was determined. The same process was repeated with seven crystals of the same substance with different masses The ratios of the masses and the corresponding potential drops for balancing currents corrected for initial current should be the same provided the temperatures are same. The results, after allowing for small temperature changes during measurements are summed up in the Table I

TABLE I

Serial no. of crystals	Mass of crystal	Potential drop in microvolts corresponding to Initial current	Balancing current	Corrected current	Ratio of potential drops	Ratio of masses	Differences
1	0 10492 gm	−53	4266	$V_1 = 4319$	$\frac{V_1}{V_2} = 1\ 3693$	$\frac{m_1}{m_2} = 1\ 3700$	− 0007
2	0.07658 „	− 53	3101	$V_2 = 3154$	$\frac{V_1}{V_3} = 1\ 6997$	$\frac{m_1}{m_3} = 1\ 6991$	+ .0006
3	0 06175 „	−52	2489	$V_3 = 2541$	$\frac{V_1}{V_4} = 1\ 8778$	$\frac{m_1}{m_4} = 1\ 8799$	− 0021
4	0 05581 „	−52	2248	$V_4 = 2300$	$\frac{V_1}{V_5} = 2\ 0905$	$\frac{m_1}{m_5} = 2.0917$	−.0012
5	0 05016 „	−53	2013	$V_5 = 2066$	$\frac{V_1}{V_6} = 2\ 4061$	$\frac{m_1}{m_6} = 2.4042$	+ .0019
6	0 04304 „	−54	1795	$V_6 = 1795$	$\frac{V_1}{V_7} = 4\ 1649$	$\frac{m_1}{m_7} = 4\ 1635$	+ .0014
7	0 02520 „	−54	0983	$V_7 = 1037$			

It will be seen from above that the reproducibility of the results are better than 0.1%

We adopted the following procedures to check the accuracy of our measurements :

a) A carefully prepared single crystal of Fe^{+3} alum belonging to the cubic class (using E Merck's G.R. quality reagent) was suspended from the balance arm in the usual manner The balancing current was very accurately measured. The temperature was measured with the thermocouple. The same process was repeated with the Merck's G.R. quality cobalt-free standard $NiCl_2$ solution of conc = 0.2590 and density = 1.2993 at 305.3°K, the mass susceptibility of which has been measured very accurately by several workers

(Weiss and Bruins, 1926, Brant, 1921; Bose, 1935; Nettleton and Sugden, 1939) and is given by the formula . $\chi \times 10^6 = \left(\frac{10160}{T} + 0.7193 - 0.486\right) c - 0.7193$ where T is the absolute temperature and c is the concentration of $NiCl_2$ in gms per gm of the solution The initial current was determined and susceptibility of Fe^{+3} alum was calculated. Any fluctuation in temperatue was accounted for. The measurements were made on 3 or 4 crystals of Fe^{+3} alum and the mean value was taken The value was corrected for diamagnetism and the mean sq. moment was determined by the formula:

$$\mu_f^2 = \frac{3k\chi_M T}{N\beta^2} = 7.995\chi_M T$$

The value of μ_f^2 is found to be 34.78 at 300°K as against earlier values 34 79 by Onnes and Oosterhuis (1926) and 34.80 obtained by Dutta Roy (1955) at 300°K. It has been shown by Van Vleck and Penney (1934) that for Fe^{+3} ion which is in the ${}^6S_{5/2}$ state, the mean susceptibility value should obey the Curie law upto $\frac{1}{T^2}$ term at least with a spin only value of the moment The small difference from the spin only value 35, can not be due to error arising from the shape effect of the single crystal since a spherical powder sample was observed to give the same value. The small departure must then be due to the deviations from the ideal S-state in consequence of configurational coupling or a small departure from Russel-Saunders coupling. However, our results agree with others to within 0 1%.

b) Cr^{+3} alum crystal also belongs to the cubic class. The same procedure was adopted and the μ^2_f value was obtained taking Fe^{+3} alum as standard

TABLE II

Results on $Ni(KSO_4)_2.6H_2O$

Serial no crystal	Mass in gms.	Potential drop corrp. to			Mol. susceptibility			Mean	Temp
		Initial current	Balancing current	Corrected current	$\chi_1 \times 10^6$	$\chi_2 \times 10^6$	$\chi_3 \times 10^6$	$\chi \times 10^6$	
1	06725	−52	2353	2405	4483	4351	4350	4398	300°K
2	05429	−52	1891	1943	4487	4355	4356	4396	300°K
3	.04670	−53	1616	1669	4482	4350	4349	4393	300°K
Powder	08844	−235	2926	3161	–	—	—	4393	300°K
						Sample Mean		4395	300°K
Krishnan *et al* (1933)	–	—	—	—	4306	4146	4152	4251	300°K

The value for Cr^{+3} alum as obtained by us, is 14 89 as against 14 92 by de Haas and Gorter (1932), after correction by Serres, and 14.91 by Dutta Roy (1956), all at 300°K, and is well within the experimental error of these authors

c) As a last check, we have measured the principal susceptibility values of $Ni(KSO_4)_2\ 6H_2O$ of monoclinic class. Taking chrome alum as standard, measurements were taken on three different single crystals of $Ni(KSO_4)_2.6H_2O$, suspended with crystallographic *b*-axis vertical. The measurements gave χ_1 for the substance. Employing the accurate anisotropy results of Dutta (1954), χ_2 and χ_3 were calculated. The mean $\bar{\chi}$ for spherical powdered samples was determined The values are given in Table II The results of Krishnan Chakravorty and Banerjee (1933) are given for comparison.

DESCRIPTION OF THE CRYOSTAT

The earlier cryostats used in this laboratory (Bose, 1947; Dutta Roy 1955) were of gas flow type in which liquid oxygen, kept in a separate reservoir, was pumped into the cryostatic chamber, evaporated and made to flow round the experimental chamber, the control of the temperature being effected partly by adjusting the flow of liquid and partly by a gas thermometer relay device The range of temperature was limited between 300°K and 82°K The control of temperature was not very fine and measurements at very small intervals of temperature could not be very conveniently undertaken. Moreover, the consumption of liquid oxygen was quite large as much of the cold was wasted.

In view of the above difficulties, we have constructed a new type of cryostat which avoids the above drawbacks and provides an extremely fine control of temperature. A liquid bath type of cryostat, instead of the flow type, has been chosen, the control of temperature being effected by varying the pressure in the vacuum jacket of the experimental tube. Provisions have been made to boil the oxygen at reduced pressure to reach temperatures below 90°K A heater has been incorporated to counteract a slight excess of cooling, thus facilitating an extremely fine control of temperature. The system offers a great economy of the liquid oxygen.

The cryostat (Fig. 2) consists of a wide-mouthed (about 10 cm inner diameter) silvered glass Dewar vessel (*D*) with a narrow tail (about 5.5 cm. outer diameter) to go between the pole pieces of an electromagnet with a pole gap of about 6 cm The wider part of the Dewar is about 16 cms long and the narrow tail about 18 cm. long. A suitable brass casing O protects the Dewar from accidental breakage. Another brass case (B) fits inside the glass Dewar and contains the refrigerant liquid oxygen, preventing breakage of the glass Dewar by direct contact with liquid oxygen refrigerant. The experimental chamber (A) is a double-walled silvered cylindrical pyrex gass tube 41 cms. in length, and of 2.6 cms. and 3 8 cms. inner and outer diameter respectively, with an inner lining of copper sheet and

outer wrapping of copper gauze (G) to maintain the temperature uniform. The inter-space of this jacket is connected to a mercury diffusion pump to maintain

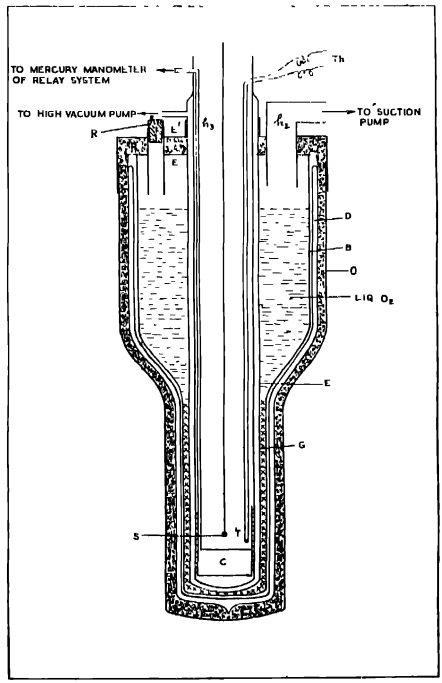

Fig. 2

a high vacuum. The interspace has a controllable leak to the fore vacuum side to control the heat leakage across the vacuum jacket. The top of the cryostat chamber is covered with a brass cap (E) fitting the inner brass casing, to which it is sealed leak tight with Wood's alloy. The outer brass casing has another cap (E') sealed to it with Wood's alloy. Each of the brass caps has three corresponding outlets. The first pair of holes h_1 are connected by a german silver tube through which liquid oxygen can be poured in and the mouth closed leak tight with a ruber stopper. Through the second pair h_2 passes a german silver tube connected to a large capacity suction pump through a pressure stabilizing bottle to make the liquid oxygen boil at reduced pressure. A sensitive differential manometer is introduced in this circuit to record the vapour pressure inside the container. The experimental tube comes out through the third tabular aperture

h_1 at the centre of the cap and is coupled to it leak-tight by a rubber band. The experimental tube then proceeds to the bottom of the balance chamber where it is sealed with picein wax. The space between the outer and inner brass caps is packed with felt and lined with an aluminium reflector to minimise the heat leakage from the top of the cryostat.

A cylindrical copper capsule (c) of about 2·4 cms. diameter and 3 cms. length fitted at the bottom of the experimental space is connected by a stainless steel capillary tube of $\frac{1}{4}$ mm. diameter to a mercury manometer system, and serves as a constant volume air thermometer temperature control unit. Two platinum electrodes fused in the manometer glass tube, one dipping inside the mercury, the other just above the mercury level, are connected to a small magnetic relay system, breaking and making the circuit of a non-inductive cylindrical nichrome 30 watt heater element kept inside the experimental chamber and fed from a 12 volt battery. The heat can be suitably controlled with an external variable loading resistance. Without using liquid oxygen in the Dewar the temperature can safely be raised to any value up to about 400°K.

The thermostatic relay-system is pre-set to any given temperature by adjusting the mass of the air in the gas thermometer. As soon as there is any fall in the temperature, the air contracts and the mercury column in the manometer closes the relay circuit through upper platinum contact which starts the heating current. When the temperature rises above the preset value, the relay circuit is broken off and the heating current stops. In this way, the temperature is controlled automatically and remains constant for sufficiently long time, within 0·01°C. This difference is not observable by changing potentiometer dial of which the least count is 2 microvolts or about 0.05°, but is detectable only with deflection of the galvanometer with no shunt, capable of detecting changes of 0·1 microvolt i.e., about 0.002°.

For temperatures below that of room, the interspace of the glass jacket is evacuated by the mercury diffusion pump until the dark stage in the attached discharge tube is observed. The cryostat chamber is then filled with liquid oxygen and the mouth is closed by the rubber cork. The temperature inside the experimental tube is then found to go down slowly at the rate of about 1° per minute. The fall of temperature can be stopped at any stage and held constant by presetting the relay. To obtain lower and lower temperature, the fine leak to the fore vacuum is opened more and more and then diffusion pump is switched off, only the backing pump is kept running. Finally, for the measurement at liquid oxygen temperature, the backing pump is also shut off and a leak to the atmosphere is introduced.

For measurements in the range of 90°K to 60°K, the liquid oxygen inlet is tightly closed by a rubber cork and the large capacity suction pump connected to the cryostat chamber is started. The pressure is adjusted and read off from

the differential manometer giving the temperature of boiling oxygen, from vapour pressure chart. Different temperatures down to about 62°K are obtained by changing the pressure with the help of a suitable leak valve in the pump circuit and using the heater coil with the help of the relay system.

THERMOCOUPLE CALIBRATION AND TEMPERATURE MEASUREMENT

The temperature in the region occupied by the crystal in the experimental chamber is measured with the help of a copper-constantan thermocouple T (Fig 2). One of the junction is located close to the crystal where the temperature is appreciably the same and the other junction is kept at the temperature of pure melting ice kept mixed with distilled water in a thermos bottle outside. The two junctions are sheathed by thin walled pyrex glass tube.

The thermocouple was calibrated in the usual manner (Bose, 1947) using a vernier potentiometer reading to 1 microvolt

The temperature — e m.f. relationship of the thermocouple is given by

$$E = at + bt^2 + ct^3 + dt^4$$

where for our thermocouple.

$$a = 41.101$$
$$b = 0.03977$$
$$c = 1.941 \times 10^{-6}$$
$$d = 4.7905 \times 10^{-7}$$

The calibration of the thermocouple was checked with the Leiden helium gas thermometer scale by comparing Leiden susceptibility measurements of ferric ammonium sulphate alum at the room-temperature, liquid ethylene and liquid nitrogen temperatures with our own. Our room temperature susceptibility is related to those at other temperatures by the formula (Bose, 1947).

$$\frac{F_T}{F_\theta} = \frac{\chi_T}{\chi_\theta}\left[1 + \frac{K_{a\theta}}{K_\theta}(1-\gamma\theta)\left(1 - \frac{\theta}{T}\right)\right] \qquad \ldots (13)$$

where χ_T and χ_θ are the gram molecular susceptibilities of the substance at temperature T and room temperature respectively, F_T and F_θ are the forces acting on the sample at these temperatures, $K_{a\theta}$ and K_θ are the volume susceptibility of air and that of the substance at room temperature θ, and γ is the coefficient of thermal volume expansion of the sample. So, the measurements of susceptibilities at other temperatures can be easily made by comparing forces on the sample at room temperature and any other temperature.

The results of the low temperature measurements of ferric ammonium alum are given graphically in the form of $p_f^2 - T$ curve (Fig. 3) which shows very close agreement with Leiden and other values.

Since the accuracy of the measurement of the balance has already been checked and can not be doubted, the temperatures at which the susceptibilities are measured fall in very well with the Leiden scale.

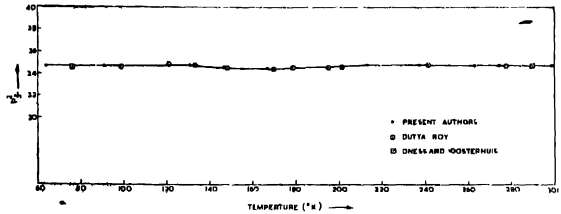

Fig. 3

Our curve for Fe^{+3} alum shows a very interesting deviation from Curie Law which, it is expected, to follow being in a ${}^6S_{5/2}$ ground state. There is a deviation in the linearity of the $p_f^2 - T$ curve with a flat minimum at about 170°K. This deviation is reproducible and exactly reversible It is already noticeable in Leiden and Dutta Roy's measurements, but no explanation of this has as yet been given.

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